(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 313 154 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **88202290.8**

(51) Int. Cl.⁴: **C23G 5/00 , B08B 7/00**

(22) Date of filing: **13.10.88**

The title of the invention has been amended (Guidelines for Examination in the EPO, A-III, 7.3).

(30) Priority: **21.10.87 BE 8701197**

(43) Date of publication of application: **26.04.89 Bulletin 89/17**

(84) Designated Contracting States: **AT BE DE ES FR GB IT LU NL**

(71) Applicant: **N.V. BEKAERT S.A.**
Bekaertstraat 2
B-8550 Zwevegem(BE)

(72) Inventor: **Chambaere, Daniel**
2171 S. Cleveland-Massillon Blvd.
Copley Ohio 44321(US)
Inventor: **Coppens, Wilfried**
Cyriel Verschaevestraat 7
B-8510 Kortrijk-Marke(BE)
Inventor: **Lievens, Hugo**
Nederzwijnaarde 45
B-9710 Gent(BE)
Inventor: **De Gryse, Roger**
Dorp 49
B-9250 Oosterzele(BE)
Inventor: **Colpaert, Alex**
Machelenstraat 26
B-9870 Zulte(BE)
Inventor: **Vennik, Joost**
Nevelestraat 102
B-9880 Aalter(BE)
Inventor: **Hoogewijs, Robert**
Pintelaan 77
B-9720 De Pinte(BE)
Inventor: **Van Wassenhove, Norbert**
Lamstraat 63
B-9220 Merelbeke(BE)

(74) Representative: **Demeester, Gabriel et al**
N.V. Bekaert S.A. Bekaertstraat 2
B-8550 Zwevegem(BE)

(54) Method and apparatus for cleaning elongate metal substrates, substrates cleaned according to this method and polymeric objects reinforced with such substrates.

(57) The invention relates to a method and apparatus for continuously cleaning a long metal substrate, such as a wire, a band, a cord, etc., the long substrate to be cleaned being led through a vacuum chamber, whereinto an inert sputtering gas, such as argon, is fed, and a sufficiently high voltage being maintained between the substrate as cathode and an anode present in the chamber so that an electric discharge takes place between the two electrodes, as a result of which the substrate is cleaned by inert gas ions precipitating on it during its passage through the vacuum chamber, and the anode being formed by at least one annular electrode, fitted in a long casing of heat-radiation transmitting material and the long substrate being led through the casing in longitudinal direction. The invention further relates

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to the thus cleaned metal substrates, as well as to the objects of polymer material reinforced therewith.

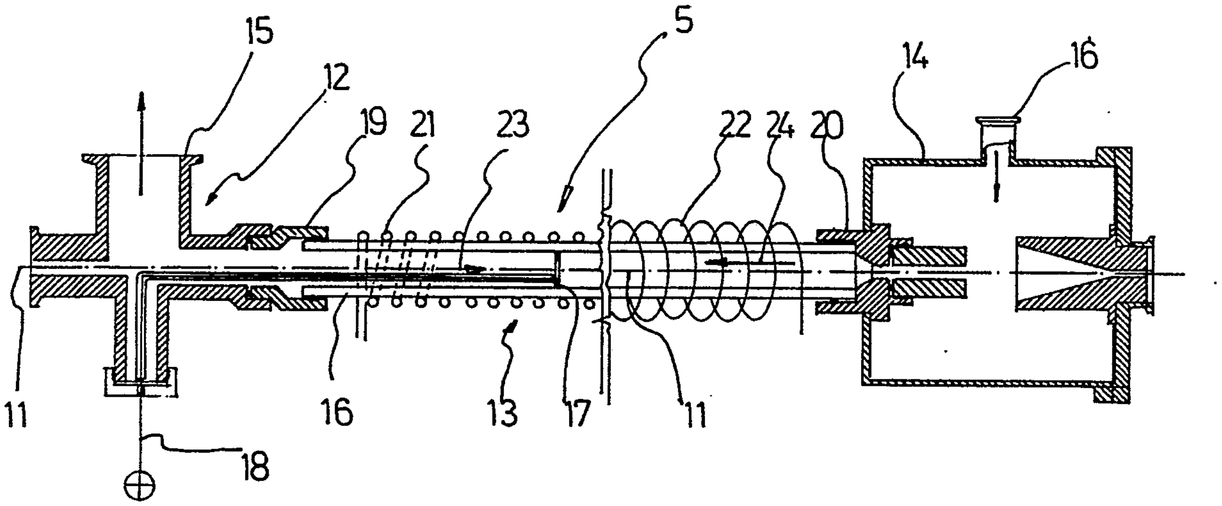

FIG. 2

METHOD AND APPARATUS FOR CLEANING A LONG METAL SUBSTRATE, SUCH AS A WIRE, A BAND, A CORD, ETC., AS WELL AS SUBSTRATES CLEANED ACCORDING TO THAT METHOD AND OBJECTS OF POLYMER MATERIAL REINFORCED WITH SUCH SUBSTRATES

The invention firstly relates to a method for continuously cleaning a long metal substrate, such as a wire, a band, a cord, etc... the long substrate to be cleaned being led through a vacuum chamber, whereinto an inert sputtering gas, such as argon, is fed, and a sufficiently high voltage being maintained between the substrate as cathode and an anode present in the chamber so that an electric discharge takes place between the two electrodes as a result of which the substrate is cleaned by inert gas ions precipitating on it during its passage through the vacuum chamber.

Such a method for cleaning long, metal substrates is described in the Dutch patent application No. 86.02760 of the present applicant.

The continous cleaning of long metal substrates is particularly important when these substrates are to be coated afterwards with a metal covering layer or when these substrates that have already been provided with a covering layer are to be embedded afterwards in a polymer material to be reinforced ; because the adhesion between substrate and covering layer, respectively between a substrate provided with a covering layer and the polymer material to be reinforced is considerably enhanced when the substrate is cleaned in a suitable way.

It has now been found that when applying the method according to the Dutch patent application 86.02760 for cleaning metal substrates, e.g. a wire, the cleaning effect of the gas discharge applied on the wire is caused by two different mechanisms. This cleaning effect is caused on the one hand by a heating of the wire, as a result of which many contaminants, those with relatively low vapour pressure such as hydrocarbons for instance, evaporate or sublimate under the influence of the increase in the temperature of the wire ; and on the other hand, by the actual ion bombardment on the wire itself or the actual sputtering, which has an excellent cleaning effect on the wire, even if the latter is kept cold or in other words if the increase in the temperature of the wire is avoided.

The heating or the increase in the temperature of the metal substrate can be very detrimental in some cases. This is particularly so when the metal substrate has already been provided with a metal covering layer, for instance of brass, zinc, etc. The said increase in temperature or the thermal cleaning has a major side effect on the metal substrate coated with brass, zinc, ..., namely, a preferential zinc segregation to the surface followed by a considerable evaporation of the zinc from the surface in the case of a brass covering layer ; a considerable evaporation of the zinc at the surface in the case of a zinc covering layer.

It is the object of the invention to provide a suitable method for continuously cleaning a long, metal substrate, the cleaning effect through the sputtering effect on the substrate being considerable, but the increase in temperature or the thermal effect being avoided almost completely.

To this end, the invention proposes for the method mentioned at the beginning, that the anode be formed by at least one annular electrode, fitted in a long casing of heat-radiation transmitting material and that the long substrate be led through the casing in longitudinal direction.

A major result hereof is a considerably lower average heating of the metal substrate as the substrate is no longer thermally protected by the surrounding anode and the casing consists of a material that transmits heat radiation. In particular, the material of the casing must transmit infrared rays. It has now been found possible with an annular electrode with an axial length of from 1 to 2 mm and a diameter of some 20 to 25 mm to select the parameters, such as pressure of the sputtering gas, feeding speed of the metal substrate, such as wire, in such a way that sputtering takes place over a substrate length that is up to 500 times and more the axial length of the annular electrode.

Preferably, the method according to the invention is applied to a steel, long substrate, such as a wire, a band, a cord, etc. that has already been provided with a covering layer of brass, zinc, etc.

With great preference, the thus cleaned steel substrate is embedded in a polymer material, such as rubber, to reinforce this polymer material.

The invention further relates to an apparatus for the continuous cleaning of a long substrate, such as a wire, a band, a cord, etc. at least comprising a chamber with means for creating a vacuum in this chamber, an anode set up in this vacuum chamber, elements for supplying an inert sputtering gas, such as argon, to this vacuum chamber, means for continuously guiding the long substrate through the high-vacuum chamber, and means for maintaining a sufficiently high voltage between the substrate as cathode and the anode present in the chamber, so that an electric discharge takes place between these two electrodes. The apparatus according to the invention is characterized in that the anode is formed by at least one annular electrode, which is fitted in a long casing of heat-radiation transmitting material.

Preferably, the long casing shows a circular cylindrical surface and is made of glass.

Finally, the invention also relates to the metal substrates cleaned in accordance with the method and in the apparatus according to the invention ; as well as to the objects of polymer material, such as rubber, that have been reinforced with such cleaned metal substrates.

The invention will be illustrated in the following description with reference to the accompanying drawing wherein :

Figure 1 shows a block diagram of a complete line, the apparatus according to the invention constituting part of the line.

Figure 2 shows a schematic longitudinal section through an apparatus according to the invention, and

Figure 3 shows an important part of the apparatus according to the invention.

In figure 1, parts of a complete line are represented with reference numbers 1 - 9, the apparatus according to the invention being represented with reference number 5. The long metal substrate to be cleaned is paid off from a reel or element of like kind in a station 1 and is led into the actual cleaning apparatus 5 via the chambers 2, 3 with valve 4, then to be rewound on a take-up reel 6 via the chambers 2′ and 3′ with valve 4′. Such a line is for instance represented in British Patent 1.362.735 wherein a vacuum space is preceded and followed by two vacuum chambers or locks.

The vacuum chambers 2 and 2′ are connected to a known roots pump 7 ; whereas the chambers 3 and 3′ are connected to a rotary valve pump 8. The actual working space or vacuum space 5 is connected to a turbomolecular pump 9. Feed-through elements 10, 10′ of suitable types are present between the atmosphere (pay-off and take-up stations 1, 6) and the chambers 2, 2′ ; respectively between the chambers 2, 3 and 2′, 3′. In addition to feed-through elements of the type 10 and 10′, there are also hermetically sealable valves 4 and 4′ between the chambers 3 and 5 and 3′ and 5, respectively.

The working of the line is as follows. A vacuum of 10^{-1} to 10^{-2} Torr is created in the chambers 2 and 2′, by means of the roots pump 7, with a flow rate of 500 m^3 per hour for instance. A still better vacuum, of 10^{-2} Torr or lower for instance, is created in the chambers 3 and 3′, by means of the pump 8, for instance with a flow rate of 10 m^3 per hour. A high vacuum, of 10^{-4} to 10^{-7} Torr for instance, is created in the vacuum space 5 by means of the turbomolecular pump 9. The valves 4 and 4′ are completely closed while a vacuum is created by pumping in the space 5. When this condition is reached, the line is ready for the method for cleaning the long substrate 11 to be started when the valves 4 and 4′ are opened.

A typical embodiment of the vacuum space or vacuum chamber 5 is schematically represented in longitudinal section in figure 2. This vacuum space 5 consists of three interconnected spaces 12, 13 and 14. The space 12 is provided with connecting elements 15 for the turbomolecular pump 9, whereas the space 14 is provided with connecting elements 16 for the supply of an inert gas, such as argon. The actual apparatus 13 for cleaning the long substrate 11 is inserted between the vacuum spaces 12 and 14.

The apparatus 13 consists of a long casing 16, preferably with a circular cylindrical surface, of a material, glass for instance, that transmits heat radiation. A circular anode 17 with insulated supply wire 18 for applying the voltage has been fitted in this casing 16. Both ends of the glass casing or tube 16 are fitted in sealing supporting elements 19, 20 in the walls of the contiguous vacuum spaces 12, 14. Cooling elements 21 have been fitted round the glass tube 16 for the cooling of the surface of the tube 16. Further, a coil 22 has been fitted round the glass tube or casing 16 to generate a magnetic field in the tube 16. For the sake of the clarity of figure 2, the cooling elements 21 and the coil 22 are only partially represented.

Figure 3 is another, detailed representation of part of the glass tube or casing 16 with the annular anode 17 set up therein with insulated supply wire 18 for applying the voltage to the annular electrode 17. The tube 16 has, for instance, a length of 500 mm and a diameter of 25 mm.

The method for cleaning a long substrate 11, such as a wire, a band, etc. is as follows. When the line is ready for the method to be started, the substrate 11 to be cleaned is led through the vacuum chamber 5 in the direction of the arrow 23. An inert sputtering gas, such as argon, is constantly fed into the vacuum chamber 5 or into the spaces 12, 13 and 14 until a pressure of between 0.01 Torr and 10 Torr is reached. A sufficiently high voltage is maintained between the annular anode 17 and the substrate 11 as cathode, so that a plasma is formed between the two electrodes, e.g. at a voltage ranging between 100 to 1000 Volt with current intensities of between 50 and 200 mA. The substrate 11 is cleaned by the inert argon ions precipitating on it from the plasma between the substrate 11 as cathode and the annular electrode 17 as anode or, in other words, the ion bombardment on the wire itself, the actual sputtering, has an excellent cleaning effect on the wire. Preferably, the substrate 11 will be kept at earth potential. The apparatus according to the invention also allows to apply triode sputtering or, in other words, it is also possible to install an additional independent source of electrons, e.g. a thermal cathode.

The method according to the invention is particularly applied to metal substrates, such as steel wires, steel cords, etc., that are provided with a covering layer o zinc, brass, etc. During cold sputtering according to the invention, the steel wires, steel cords, etc. provided with a covering layer are effectively cleaned without the temperature of the substrate 11 being raised considerably. To prevent a temperature rise in the space 13, this space 13 is also cooled by means of cooling elements 21.

A further characteristic of the method according to the invention consists in that the inert sputtering gas, such as argon, is led through the casing or tube 16 in the direction of the arrow 24, or this means that the substrate 11 and the sputtering gas are guided in opposite direction inside the vacuum space 13.

The method according to the invention is further characterized in that the cleaned substrate 11 is embedded in a vulcanizable elastomer, such as rubber, preferably immediately after the cleaning.

Still many improvements can be made within the scope of the invention, with regard to both method and apparatus. For instance, a coil 22 is fitted round the tube 16 to generate a magnetic field in the space 13, thus increasing the probability of ionization of the sputtering gas. This leads to a higher plasma density, resulting in a further improvement of the quality of the cleaned substrate 11.

Claims

1. Method for the continuous cleaning of a long metal substrate (11), such as a wire, a band, a cord, etc., the long substrate (11) to be cleaned being led through a vacuum chamber (5), whereinto an inert sputtering gas, such as argon, is fed, and a sufficiently high voltage being maintained between the substrate (11) as cathode and an anode (17) present in the chamber so that an electric discharge takes place between the two electrodes (11, 17) as a result of which the substrate (11) is cleaned by inert gas ions precipitating on it during its passage through the vacuum chamber (5), characterized in that the anode (17) is formed by at least one annular electrode, fitted in a long casing (16) of heat-radiation transmitting material and in that the long substrate (11) is led through the casing (16) in longitudinal direction.

2. Method according to claim 1, characterized in that the long casing (16) is a circular cylindrical surface.

3. Method according to claim 1 or claim 2, characterized in that the long substrate (11) is set at earth potential.

4. Method according to one or more of the preceding claims 1 - 3, characterized in that the inert sputtering gas and the substrate (11) to be cleaned are led through the long casing (16) in opposite direction.

5. Method according to one or more of the preceding claims 1 - 4, characterized in that the long substrate (11) is made of steel.

6. Method according to claim 5, characterized in that the steel substrate (11) is provided with a covering layer.

7. Method according to claim 6, characterized in that the covering layer is made of brass or zinc.

8. Method according to one or more of the preceding claims 1 - 7, characterized in that the long casing (16) is made of glass.

9. Method according to one or more of the preceding claims 1 - 8, characterized in that the thus cleaned substrate is embedded in a polymer material, such as rubber.

10. Apparatus for the continuous cleaning of a long substrate (11), such as a wire, a band, a cord, etc. at least comprising a chamber (5) with means for creating a vacuum in this chamber, an anode (17) set up in this vacuum chamber (5), elements for supplying an inert sputtering gas, such as argon, to this vacuum chamber (5), means for continuously guiding the long substrate (11) through the high-vacuum chamber (5), and means for maintining a sufficiently high voltage between the substrate (11) as cathode and the anode (17) present in the chamber, so that an electric discharge takes place between these two electrodes, characterized in that the anode (17) is formed by at least one annular electrode (17), which is fitted in a long casing (16) of heat-radiation transmitting material.

11. Apparatus according to claim 10, characterized in that the long casing (16) is a circular cylindrical surface.

12. Apparatus according to claim 10 or claim 11, characterized in that the long casing is made of glass.

13. Apparatus according to one or more of the preceding claims 10 - 12, characterized in that cooling elements (21) have been fitted round the long casing (16).

14. Apparatus according to one or more of the preceding claims 10 - 13, characterized in that a coil (22) has been fitted round the long casing to generate a magnetic field.

15. Apparatus according to one or more of the preceding claims 10 - 14, characterized in that the vacuum chamber (5) consists of three intercon-

nected spaces (12, 13, 14), viz. the long casing (16) of heat-radiation transmitting material connected at both ends to a vacuum space (12, 14).

16. Apparatus according to claim 15, characterized in that the ends of the long casing (16) are fitted in sealing supporting elements (19, 20) in the walls of the contiguous vacuum spaces (12, 14).

17. Apparatus according to claim 15 or claim 16, characterized in that the first vacuum space (12) contiguous to the long casing is provided with connecting elements (15) for a vacuum pump and in that the second vacuum space (14) contiguous to the long casing is provided with a supply inlet for inert gas.

18. Metal long substrate, characterized in that the substrate is cleaned by applying the method according to one or more of the preceding claims 1 - 9.

19. Metal long substrate according to claim 18, characterized in that the substrate is made of steel.

20. Metal long substrate according to claim 18 or claim 19, characterized in that the substrate is provided with a covering layer.

21. Metal substrate according to claim 20, characterized in that the covering layer is chosen from brass and zinc.

22. Object of polymer material, such as rubber, synthetic material, characterized in that the object is reinforced with metal, long substrates obtained according to one or more of the preceding claims 18 - 21.

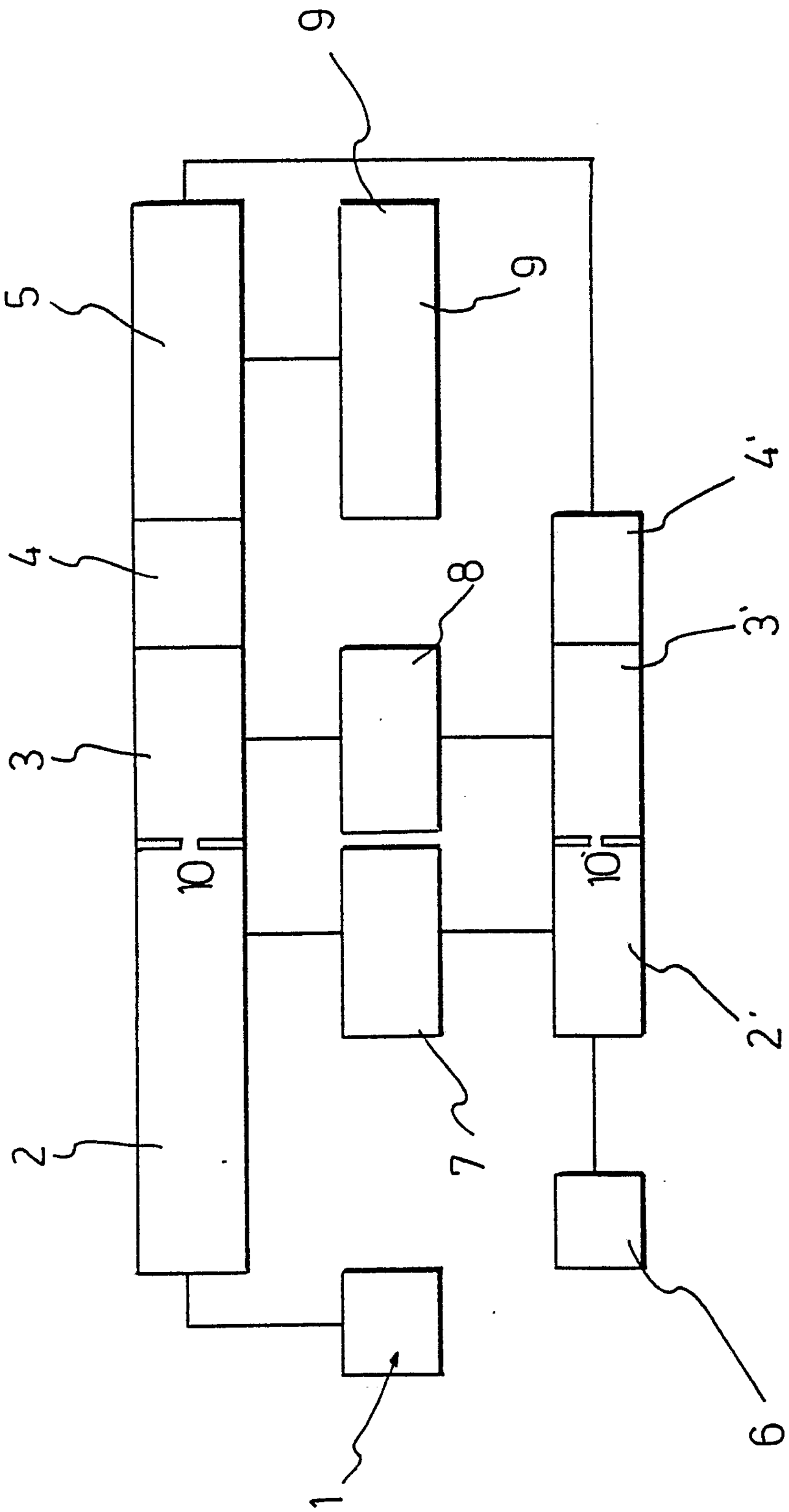

FIG.1

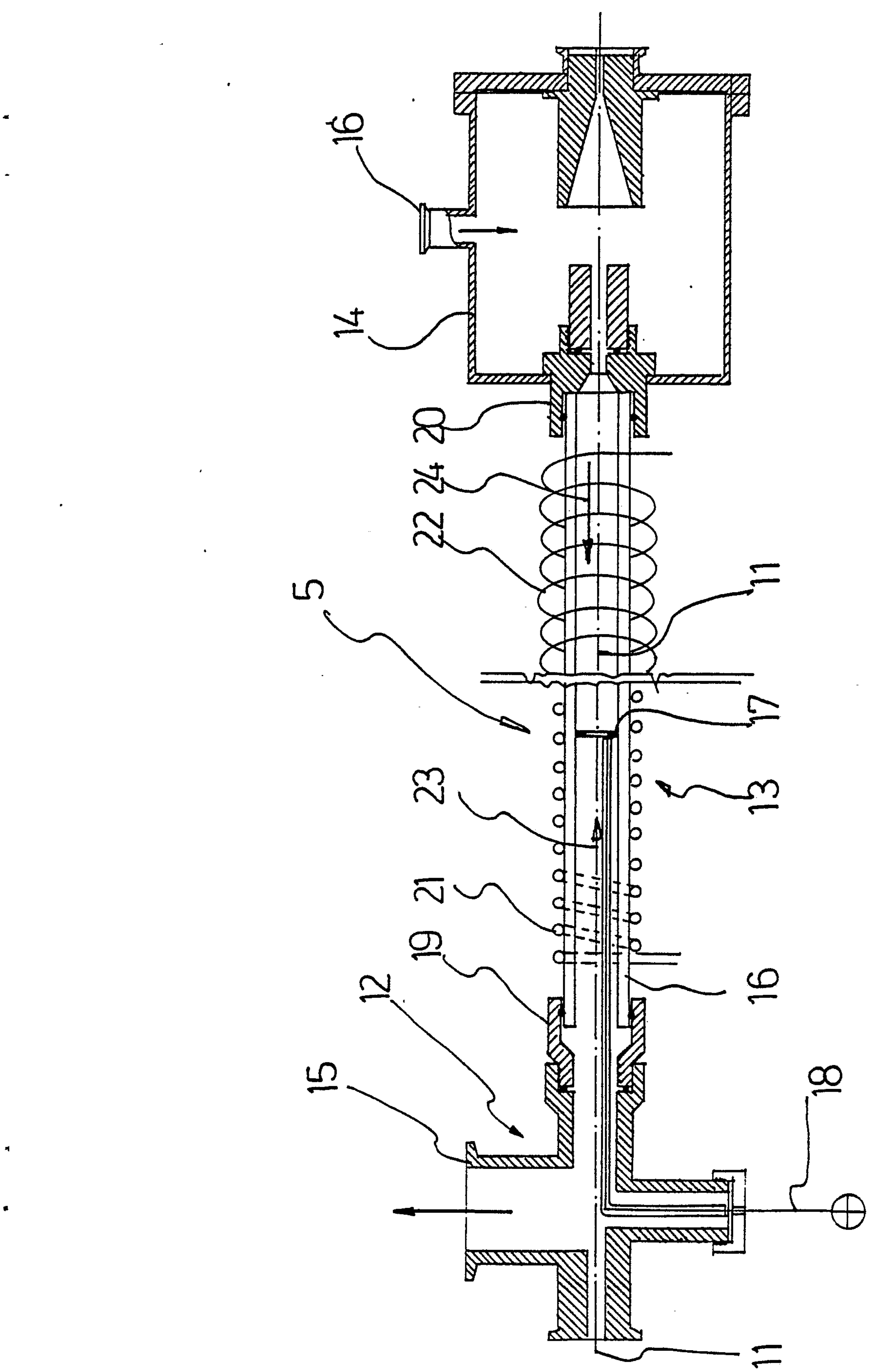

FIG. 2

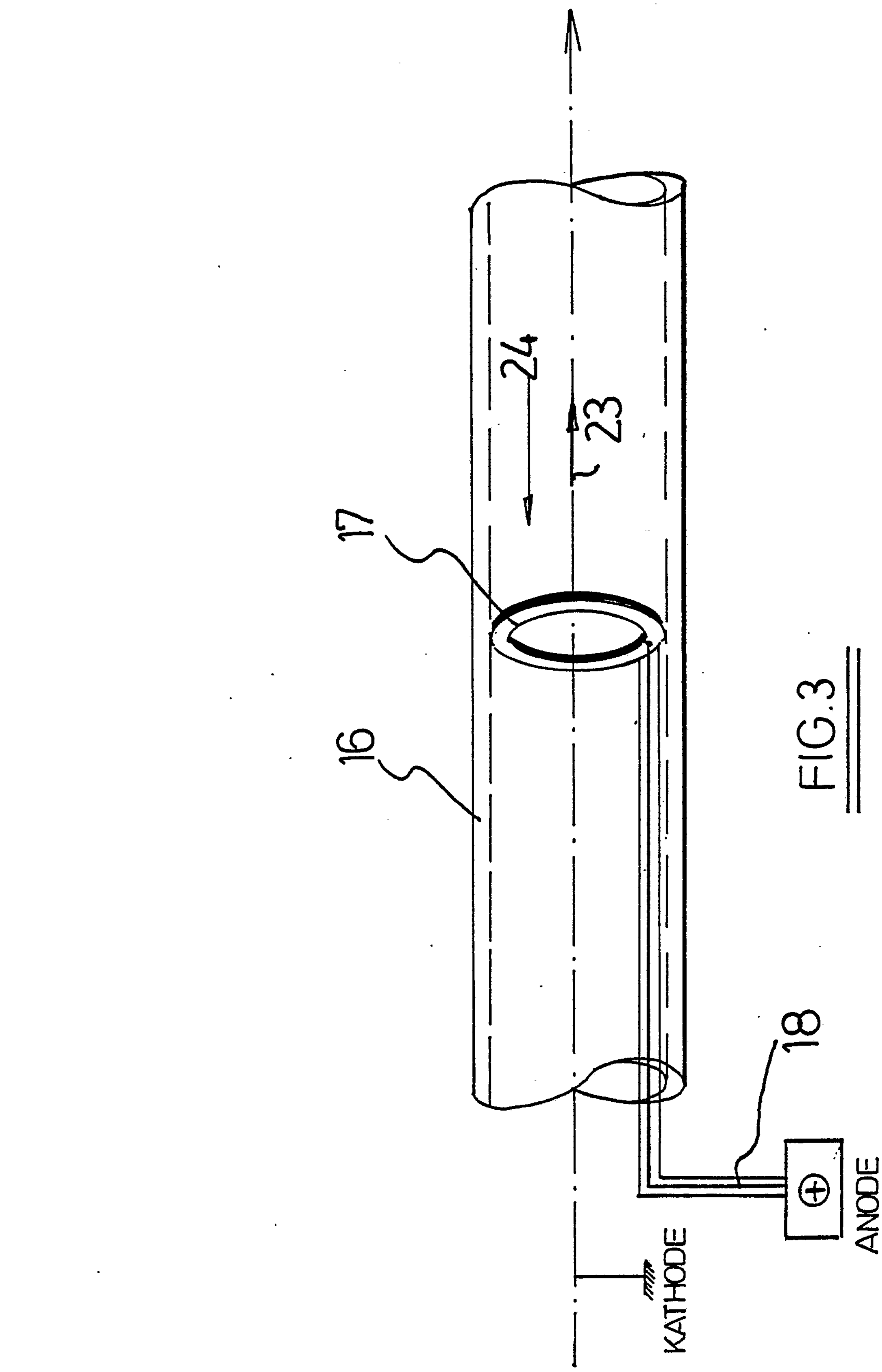

FIG.3

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EUROPEAN SEARCH REPORT

Application Number

EP 88 20 2290

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	DE-B-1 283 645 (UNION CARBIDE) * Claims 1,2,4,5; column 3, lines 29-46 *		C 23 G 5/00 B 08 B 7/00
A	FR-A-1 492 429 (LIBBEY-OWENS-FORD GLASS CO.)		
A	GB-A- 948 554 (J.E. HARLING)		
A	PATENT ABSTRACTS OF JAPAN, vol. 4, no. 173 (C-32)[655], 29th November 1980; & JP-A-55 110 782 (HITACHI SEISAKUSHO K.K.) 26-08-1980		
A	CHEMICAL ABSTRACTS, vol. 90, no. 24, June 1979, page 242, no. 190706p, Columbus, Ohio, US; & JP-A-79 01 242 (AGENCY OF INDUSTRIAL SCIENCES AND TECHNOLOGY) 08-01-1979		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 23 G 5/00 B 08 B 7/00 C 23 C 16/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23-01-1989	TORFS F.M.G.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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